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EFFECT OF LOW DENSITY  
INERT GAS FLUSH ON  
OXYGEN - COLUMBIUM REACTION  
AT 1500 °F to 2000 °F

Final Quarterly Report

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## Introduction

The study of a low density gas flush to obtain and maintain a high purity test atmosphere, shows promise of reducing the cost of ground testing of nuclear space power plants. The particular situation studied in this program involves the use of high purity argon at a reduced pressure and to protect a columbium - 1% zirconium alloy heated to 1850° to 2000° F.

The use of commercially available argon and oil sealed mechanical vacuum pumps has resulted in a test area impurity concentration of 3 ppm at 1 torr total pressure. This is equivalent to an impurity partial pressure of 3 ( $10^{-6}$ ) torr. While this impurity pressure is low enough to test many materials for reasonable time periods, an impurity partial pressure of  $10^{-8}$  to  $10^{-9}$  torr is required for long term creep tests of the highly reactive refractory metal alloys. The purpose of this phase of the investigation was to purify gases to concentrations of less than 1 ppm and to determine the impurities.

A two-stage magnetic deflection mass spectrometer was designed, constructed and evaluated for analysis of impurities in a gas stream. The equipment is capable of detecting impurities in a gas stream.

The designed gas purification system was demonstrated to be capable of reducing the impurity content of all gases below .3 ppm with the exception of the CO peak. The maximum impurity content of CO was 1 ppm.

The combination of the purification system and the analysis equipment permit the development of the program to obtain impurities corresponding to  $10^{-7}$  to  $10^{-8}$  torr.

### Technical Discussion

To obtain a high resolution, analytical mass spectrometer, three factors must be considered:

1. Sufficient signal strength (sensitivity) to detect the trace gases while operating the system at a pressure low enough to prevent defocusing of the ion beam must be provided.
2. Control of background gases in the analysis system to avoid output signals which mask the detection of trace gases.
3. Minimizing spreading of the spectrum at pressure levels corresponding to 1-50 ppm due to ion scattering, Aston banding or ion reflections.

Generally, adequate resolution can be obtained since contaminant gases are of low molecular weight (usually less than 100). The following three sections discuss the factors listed above in more detail.

### Sensitivity

The standard method of evaluating the sensitivity of a mass spectrometer measures the amount of ion current per unit of pressure (expressed as amps/torr). A typical value for mass spectrometers is  $10^{-5}$  amps/torr. If the spectrometer is operated at a total pressure of  $10^{-5}$  torr, the total ion current would be  $10^{-10}$  amps. A constituent with a concentration of one part per million would give a signal output of only  $10^{-16}$  amps, which is too low a value for normal electronic amplifiers. To overcome this difficulty, electron multipliers, which provide a gain of  $10^5$  are used. An input of  $10^{-11}$  amps to the electronic amplifier can then be measured. Since an electronic amplifier readily measures current of  $10^{-13}$  amps without background noise interference, partial pressures of .01 parts per million may be detected. To obtain the high gain of  $10^5$  for the electron multiplier, it must be operated at voltages in the range of 3000 to 4000 volts. The maximum operating pressure of a multiplier is about  $10^{-5}$  torr to avoid electrical breakdown in the high voltage field.

However, even at this pressure, the noise is increased considerably over that obtained at low pressures, see Fig. 1. The noise level in the figure is abnormally high for this multiplier. Typical values were between 1 to  $3 \times 10^{-12}$  amps at 3100 volts. The increase with pressure is quite typical and has been noticed visually over pressure ranges down to  $10^{-9}$  to  $10^{-10}$  torr. This suggests the current may be related to some type of a discharge phenomena, but this has not been proven.

Sensitivity of the spectrometer was checked for N<sub>2</sub>, argon and water vapor. At the normal emission current of 1.5 ma at 35 eV, the following values were found at a pressure of 1 to 5 x 10<sup>-5</sup> torr:

Argon	.3 amps/torr
Nitrogen	3 amps/torr
Water	2 amps/torr

A further gain in sensitivity was obtained by operating the ion source region at a higher pressure, while still maintaining the electron multiplier region at pressures below 10<sup>-5</sup> torr. The source region of the equipment was operated at pressures as high as 5 x 10<sup>-4</sup> torr while maintaining the required resolution and performance of the mass spectrometer, thus allowing for a considerable gain in sensitivity, and the ability to operate further above the noise level of the electronic amplifier. As an example, a .01 part per million concentration at a total pressure of 5 x 10<sup>-4</sup> torr in the source region produced a current input to the electron multiplier of 5 x 10<sup>-17</sup> amps for the spectrometer sensitivity of 10<sup>-5</sup> amps per torr. The electron multiplier gain of 10<sup>5</sup> resulted in an amplifier input signal of 5 x 10<sup>-12</sup> amps, which is a reasonable value for operation above the noise level.

#### Background Gases

The use of high speed pumping systems and good ultra high vacuum techniques are a mandatory condition in order to minimize the effect of background system gases.

The equipment was baked at 400 °C in order to thoroughly degas the interior surfaces. Once the system was cleaned by a 400 °C bake, a 100 °C bake removed any trace impurities.

### Spectrum Spreading

A perfect mass spectrometer would focus all ions of a given specie and not permit any ion of a different mass to be collected. In actual practice, a certain amount of defocusing does occur as a result of two principal conditions. One is that ions which are formed in the source may randomly collide with neutral gas molecules and are deflected slightly from their normal path, resulting in ions which are collected at a lower energy than their sister ions of the same mass. Second, an ion striking the walls of the spectrometer tube may be reflected into the collection system, resulting in a false broad peak in a particular region of the spectrum. Generally, these two factors are of little concern until one wishes to analyze or detect trace impurities. In this situation, since it is necessary to operate at relatively high pressures, there is a higher probability of an ion striking the relatively plentiful molecules. In addition, the high ion beam density of the principal gas results in more ions being deflected from both the walls and from neutral molecules, to produce false peaks or bands of peaks in different parts of the spectrum.

The result is seen in Fig. 2. The spectrum was obtained from the single stage magnetic deflection spectrometer used in Phase I of the contract. It has the same performance characteristics as the double stage.

Intermolecular collision forming low energy ions is a process which occurs at a rate proportional to the square of the pressure. This is true if the following reasoning is used.

The number of ions formed is:

$$N = k_1 P$$

where  $N$  = rate of ions formed by electrons

$k_1$  = constant, a function of emission current, geometry, etc.

$P$  = source pressure

The number of intermolecular ions formed, i.e., ions formed by ion-molecular collisions is,

$$n = k_2 NP$$

where  $k_2$  = constant, a function of geometry

$n$  = number of ions formed due to intermolecular collisions

Therefore,

$$n = k_1 k_2 P^2$$
$$n = K P^2$$

The band due to ion reflections would react in a manner directly proportional to pressure.

The portion of the spectrum in the region 22 - 24 followed a  $P^2$  law while most of the rest of the spectrum obeyed a  $P$  law.

A spectrum taken with the double deflection spectrometer is shown in Fig. 3. The total pressure and sensitivity is approximately the same as that shown for the single stage spectrometer.

The ion-molecular scattering problem was minimized by reducing the path length that an ion travels in the high pressure region. The maintenance of a pressure drop between the source

region and the main tube region of the spectrometer tube reduced the path length. The principal path length of the ion is then in a region of reduced pressure and longer mean free path.

Ion-wall reflections were minimized by using a physically large spectrometer housing and by installing ion stops which trap molecules attempting to enter the collection slit from improper angles.

### Resolution

It was decided that the instrument should be a symmetrical 2" radius of curvature with .007" wide source and intermediate slit. Also, the collector slit was made .030" to facilitate magnet alignment. A resolution of 7 parts per thousand would be obtained if the slit width and radius of curvature were the only influencing factors. The argon 40 peak appeared triangularly shaped when the signal was approximately one full scale on the recorder chart. Further examination of the peak revealed an assymetric shape (see Fig. 4). The high mass side of the peak is very abrupt. The low mass side had a long tail extending down into the 34 to 36 regions. This type of phenomena could occur for at least two reasons: improper magnet alignment or low energy argon 40 ions. At a peak height of 1.5% of the total height, the width represented 7 parts per thousand.

## Performance

Figs. 5 - 7 are examples of the performance of the instrument. Fig 5a is a spectrum of a  $N_2$ ,  $O_2$ , argon mixture with the total pressure being approximately  $3 \times 10^{-6}$  torr. The trace of oxygen and argon can be just detected. Fig. 5b is an increase in sensitivity of 100 : 1. Only the region between masses 32 and 40 are seen. A small peak at mass 36 is detectable, representing approximately 3% of the 40 peak. Fig. 6 shows the same mass range at sensitivities  $10^3$ ,  $10^4$  and  $10^5$  times greater than that shown on Fig. 5a. Fig. 7a shows a peak corresponding to .200 ppm of krypton in the sample. Figs. 7b and 7c show the mass range between 46 and 50. A 10% of full scale deflection represents .020 ppm. A reduction in amplifier band width and scan speed would enable detection of .010 ppm.

Fig. 8 is a normal spectrum from the equipment used for this study.

## Gas Purification System

### Introduction

The gas cleaning system worked well for all gases except CO. Water, CO,  $CO_2$  and hydrogen were the only gases detected at concentrations greater than .02 ppm. All gases except CO were below .3 ppm. The behavior of CO is peculiar and its source could not be positively identified.

### Description of the Gas Purification System

The system consisted of a titanium foil getter and a molecular sieve absorption column. The entire system was bakeable to 300 °C and did not have any organic seals or valves except the

pressure regulator. The pressure regulator was designed for high purity gas service. During normal operation, the gas would travel from the gas storage cylinder through the molecular sieve column to the titanium getter. At this point, a throttle valve permitted sampling the gas to the mass spectrometer analysis system.

The molecular sieve column contained 7.5 lb. of zeolite. This is sufficient to maintain the equilibrium pressure of water vapor below  $10^{-6}$  torr for a period of 1000 hours at a flow rate of 1 torr-liter/sec. The container for the sieve was surrounded with an oven capable of raising the temperature to 300 °C. The oven also is suitable for containing dry ice to lower the temperature to approximately -100 °F.

Strips of .016 x 1" x 12 " of titanium were wound in the shape of helices. After winding, the titanium was degreased in acetone and cleaned in a 1 HF - 4 HNO<sub>3</sub> - 15 H<sub>2</sub>O mixture. During normal operation, the titanium is heated to 750 °C to getter the N<sub>2</sub>, O<sub>2</sub>, CO and CO<sub>2</sub>.

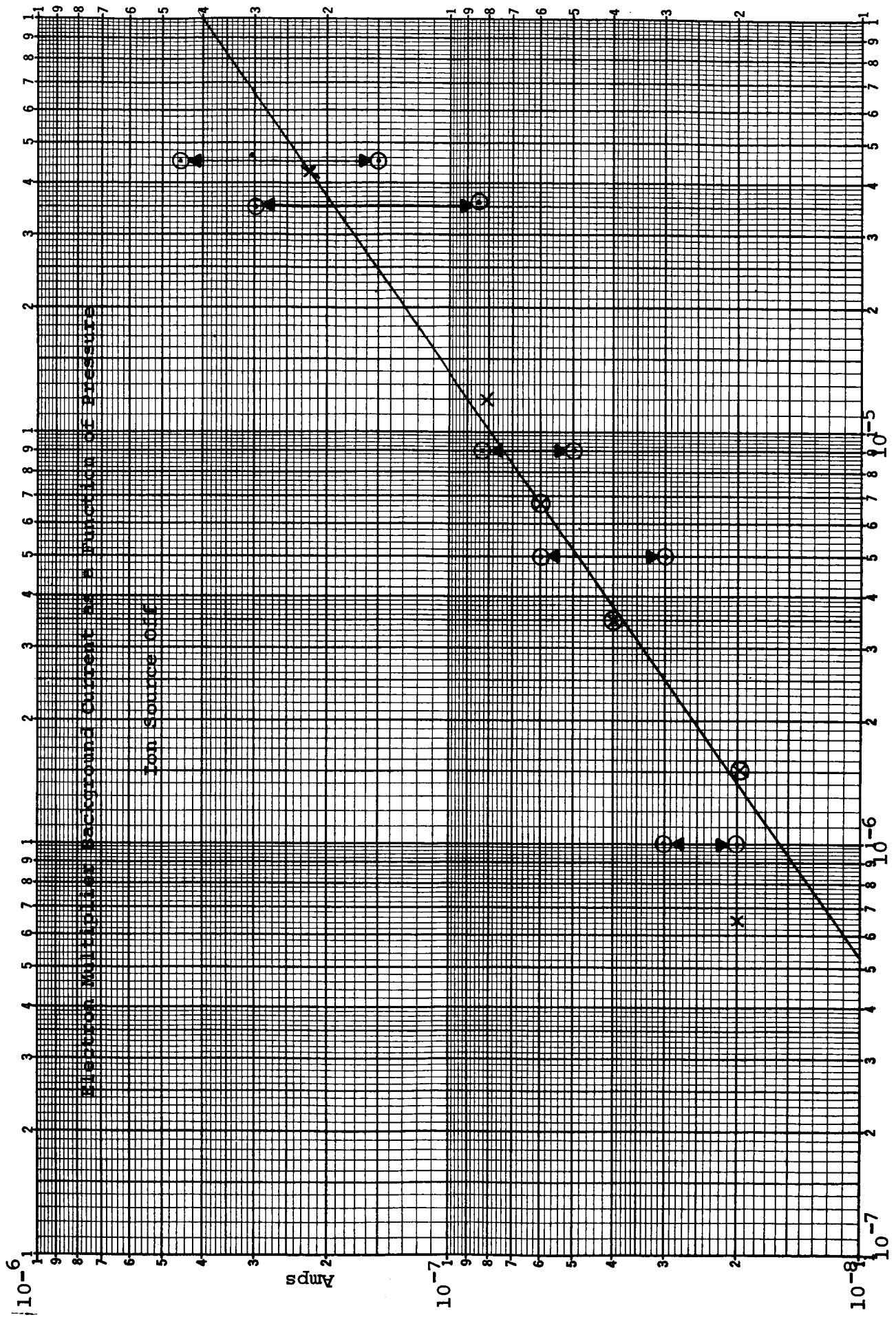
Initially, the system is evacuated and a pressure of 100 microns is maintained by a throttling valve. This prevents any adsorbed gases from traveling from the zeolite to the titanium foil. Once pressure stability is attained, the system is baked at 300 °C, with the exception of the titanium getter. The getter is heated slowly to 900 to 950 °C. The initial firing of the getter caused evolution of large quantities of hydrogen. The first analysis at this temperature revealed 1% hydrogen in the argon. Subsequent degassing and operation of the titanium at 750 °C caused the hydrogen to be an insignificant (less than 3 ppm) contribution to the argon purity. This level of hydrogen

in the purge gas was not considered important and no attempt was made to further decrease the level.

The system was initially degassed at 300 °C for one week. An overnight degas was sufficient for the subsequent exposures to atmosphere to lower the impurity level to a satisfactory point.

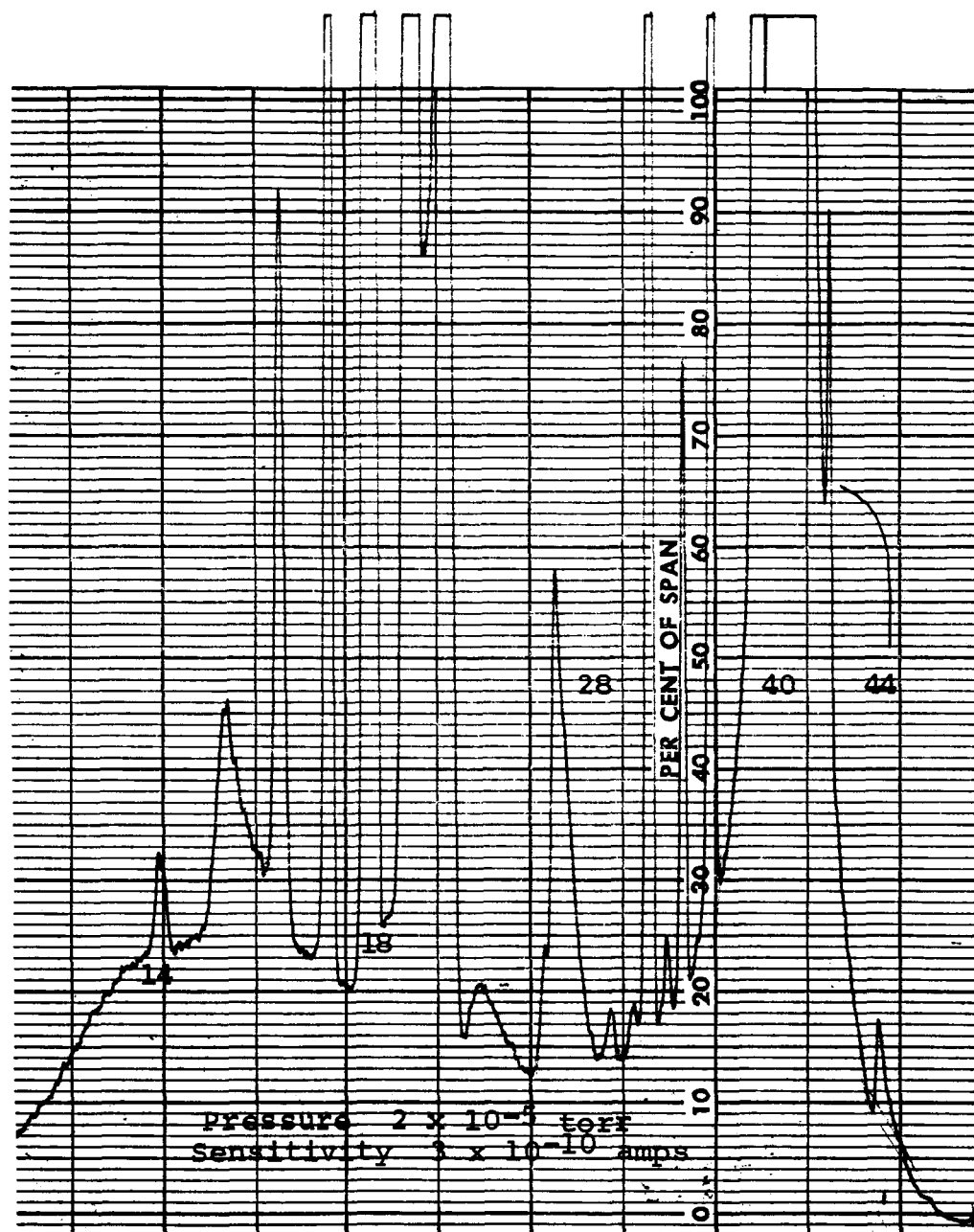
Experimentation revealed the benefit of reducing the molecular sieve temperature to -100 °F.

Figs. 9 and 10 are spectra of the gas after it has been purified. One analysis is performed at  $7 \times 10^{-5}$  and the other at  $5.5 \times 10^{-5}$  torr. There are only a few peaks present. Full scale sensitivity is approximately 2 ppm for the analysis at  $7 \times 10^{-5}$  torr and 2.5 ppm taken at  $5.5 \times 10^{-5}$  torr. Sensitivities of .14 ppm and .25 ppm respectively of water vapor are shown on the two respective curves. On all of the spectra taken, a peak corresponding to a mass to charge ratio of 16, occurs. The magnitude of this peak did not have any relationship to the 28 or 44 peak. It was attributed to electrons striking adsorbed oxides on the metallic surfaces. Carbon dioxide was present at .27 ppm. It is not seen on the spectrum taken at  $7 \times 10^{-5}$  torr due to the time response of the amplifier after saturating with the high argon signal.



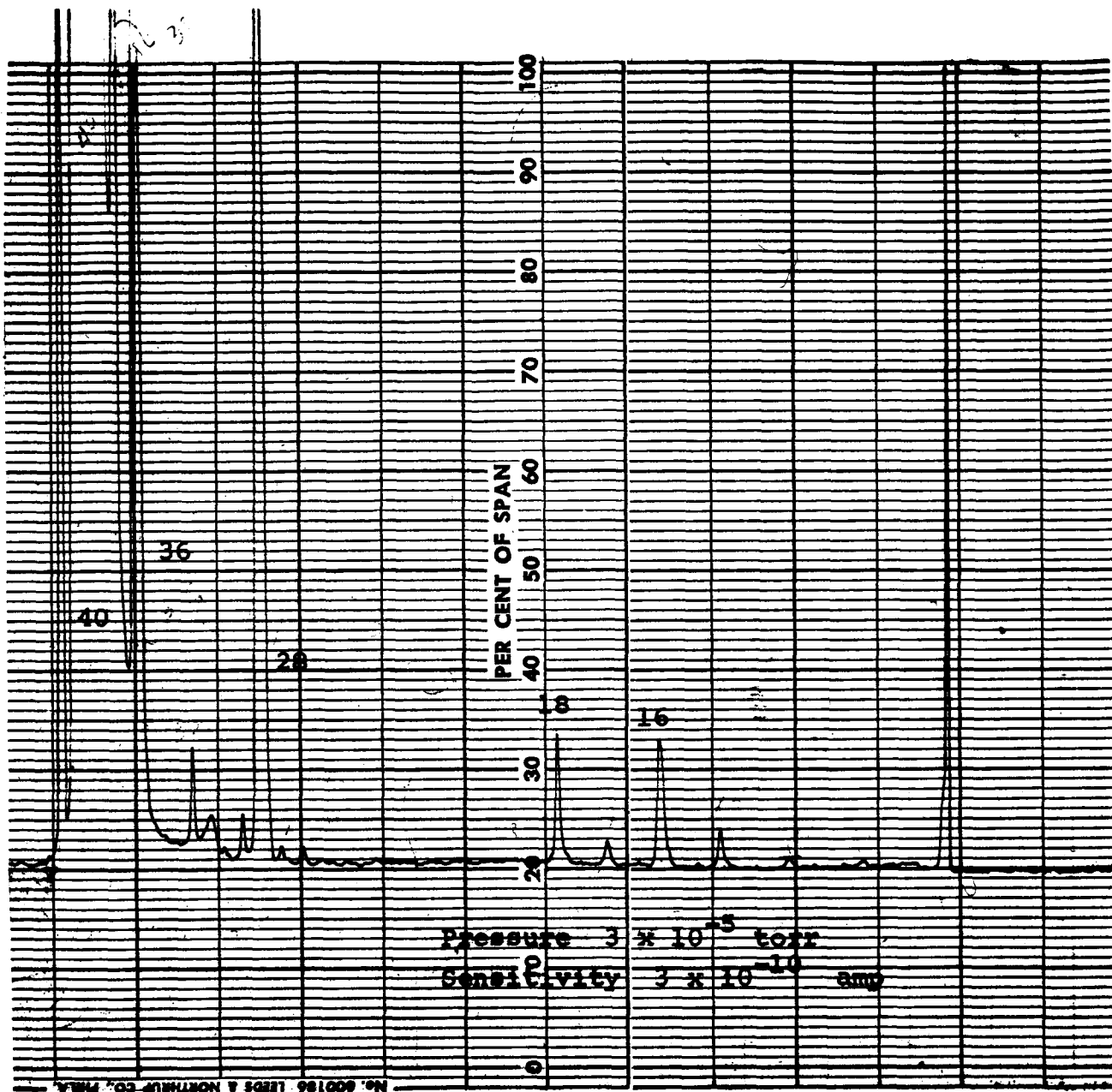
Pressure (torr)

Fig. 1



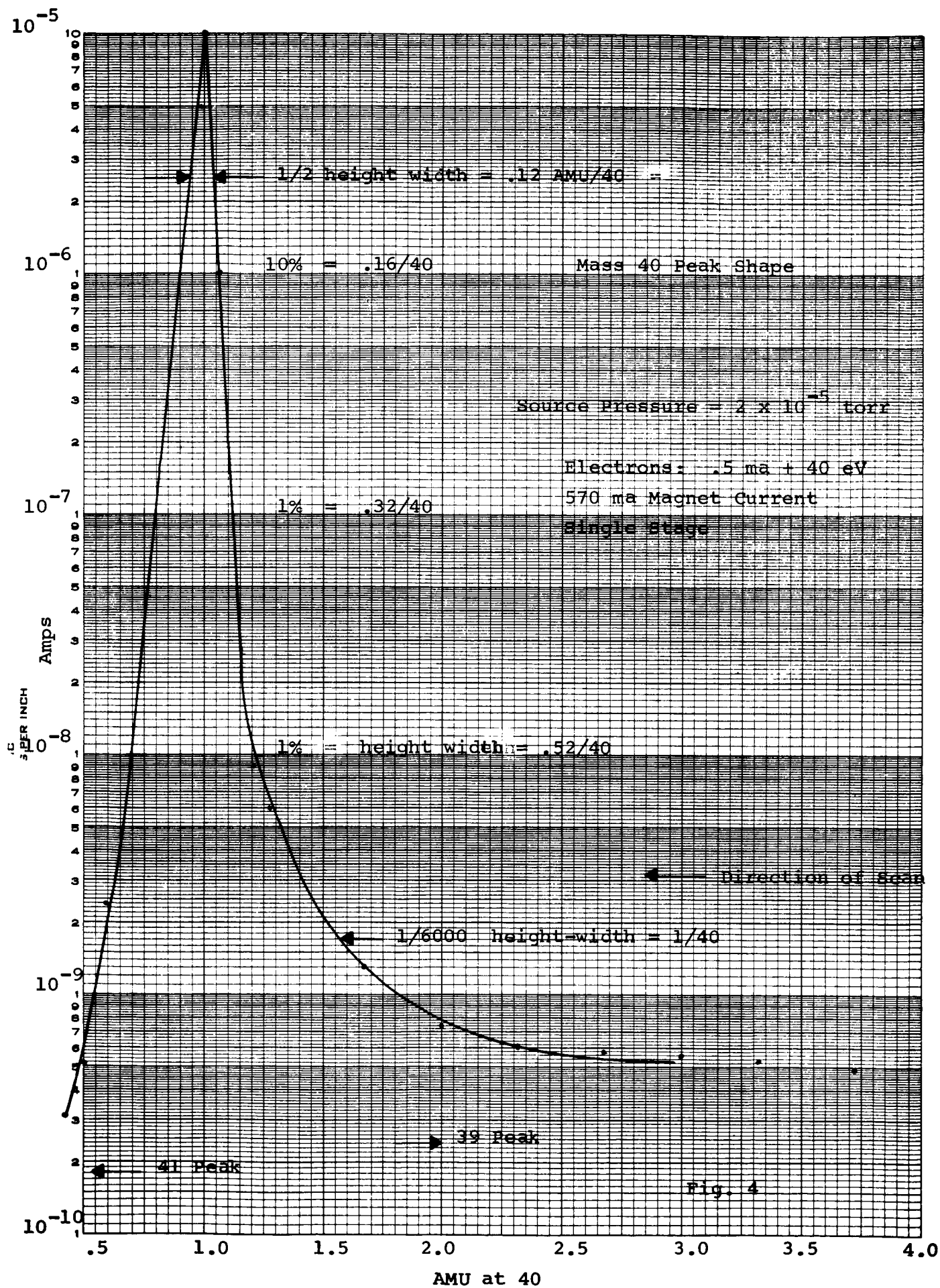
Spectrum Taken from Single Stage 2" Radius of  
Curvature Magnetic Deflection  
Spectrometer

Fig. 2



Spectrum from Double Stage Magnetic Deflection Spectrometer

Fig. 3



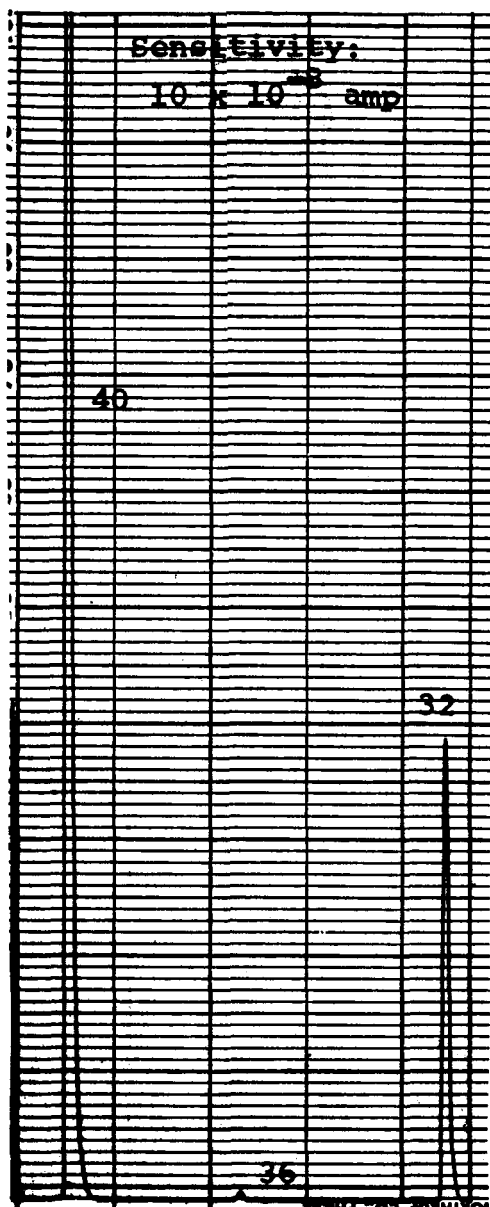


Fig. 5b

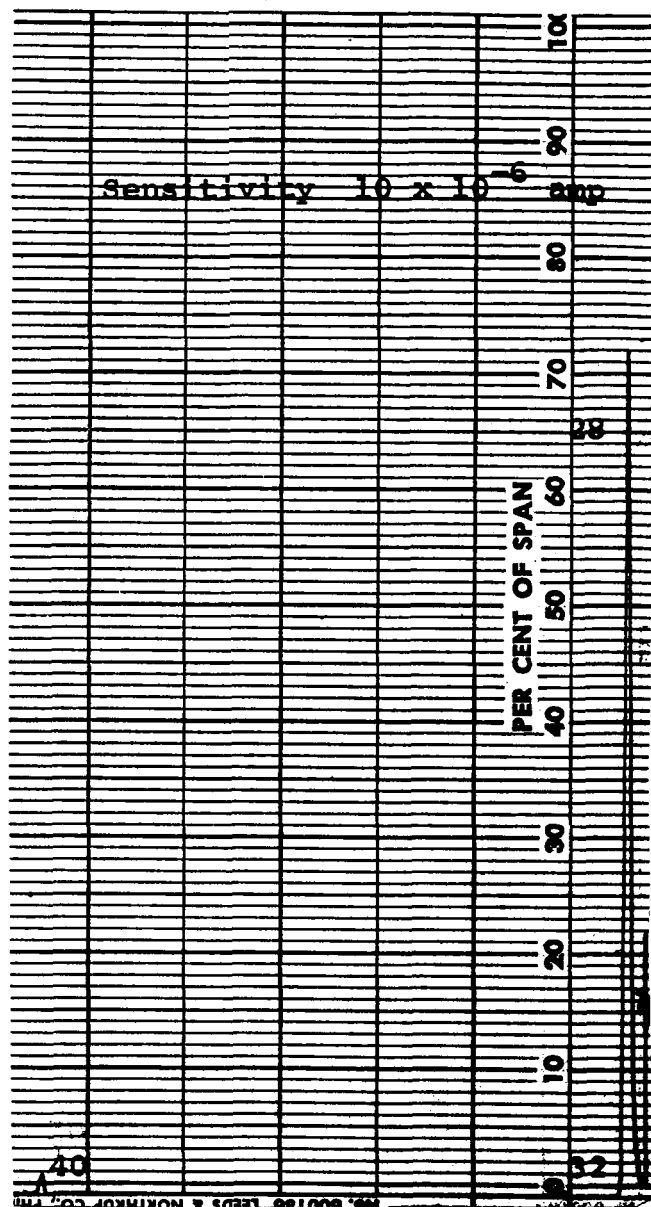
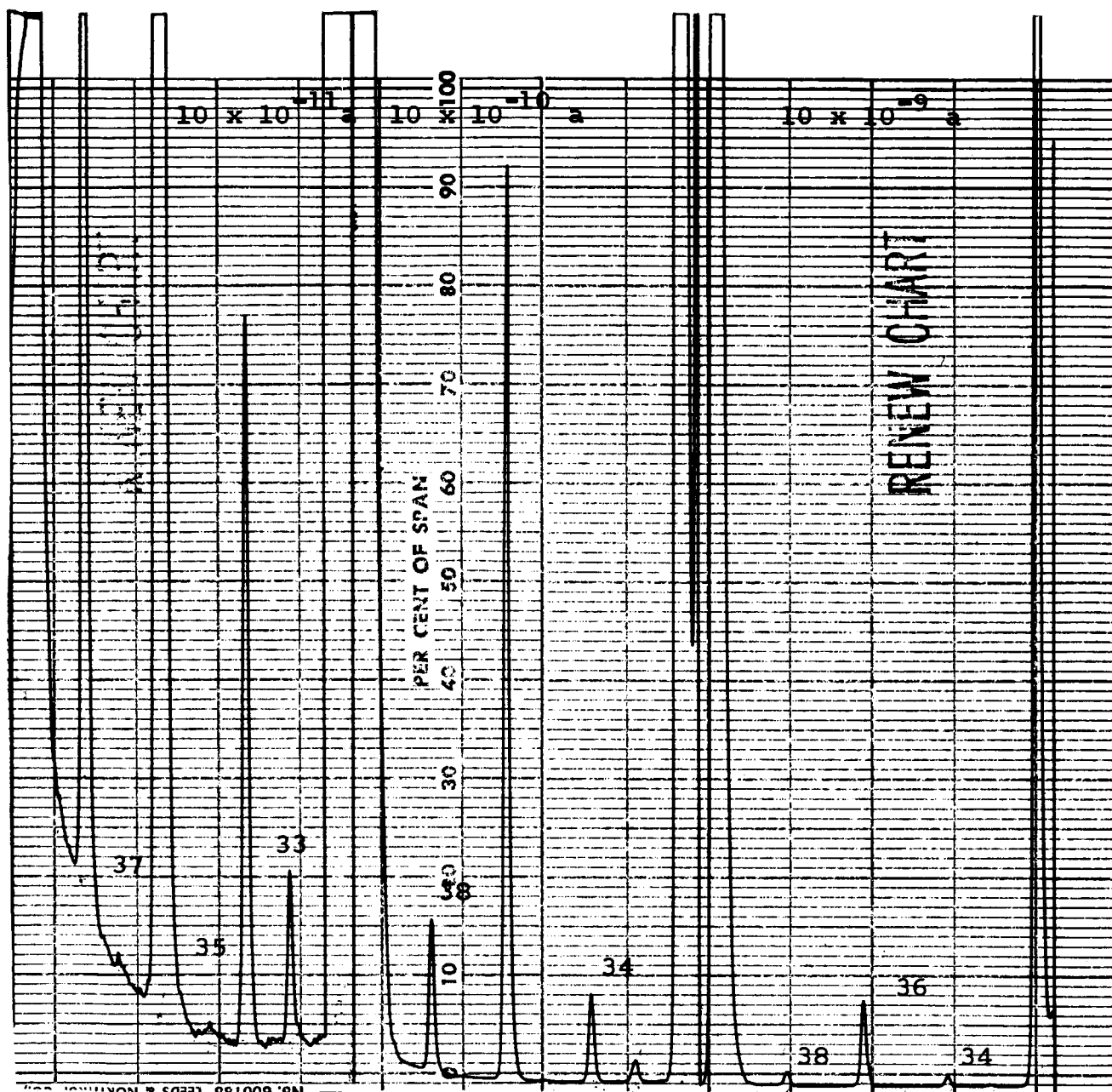


Fig. 5a

Spectra of  $N_2$ , Ar,  $O_2$  Mixture at Various Sensitivities



Spectra of  $\text{N}_2$ , Ar and  $\text{O}_2$  at Various Sensi-  
tivities

Fig. 6

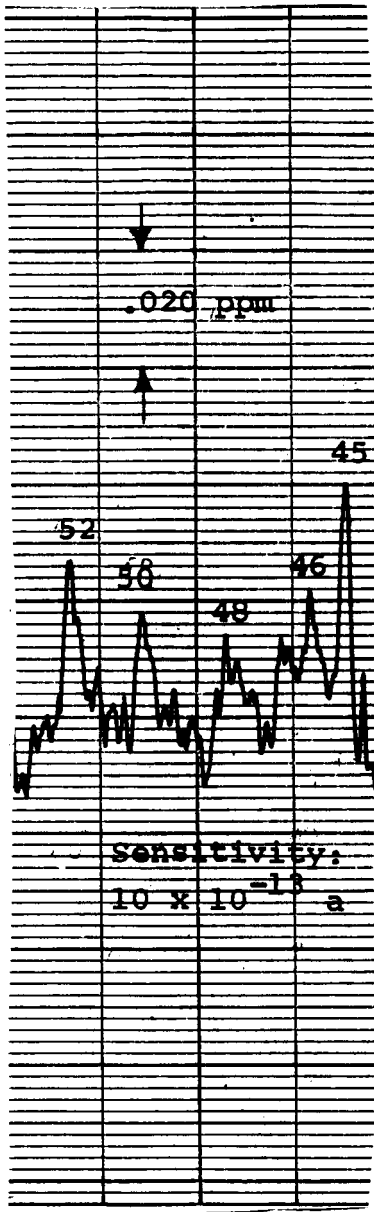


Fig. 7b

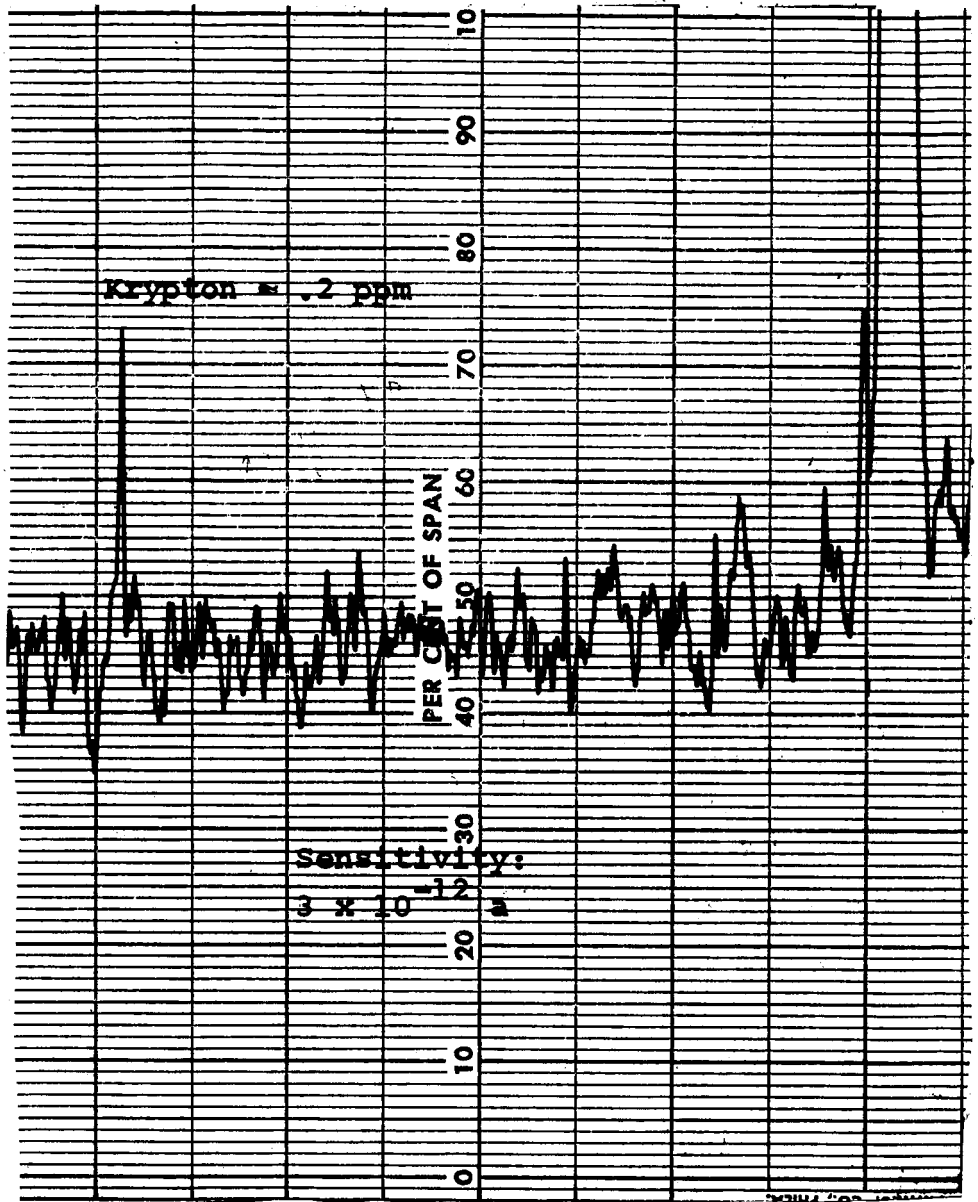
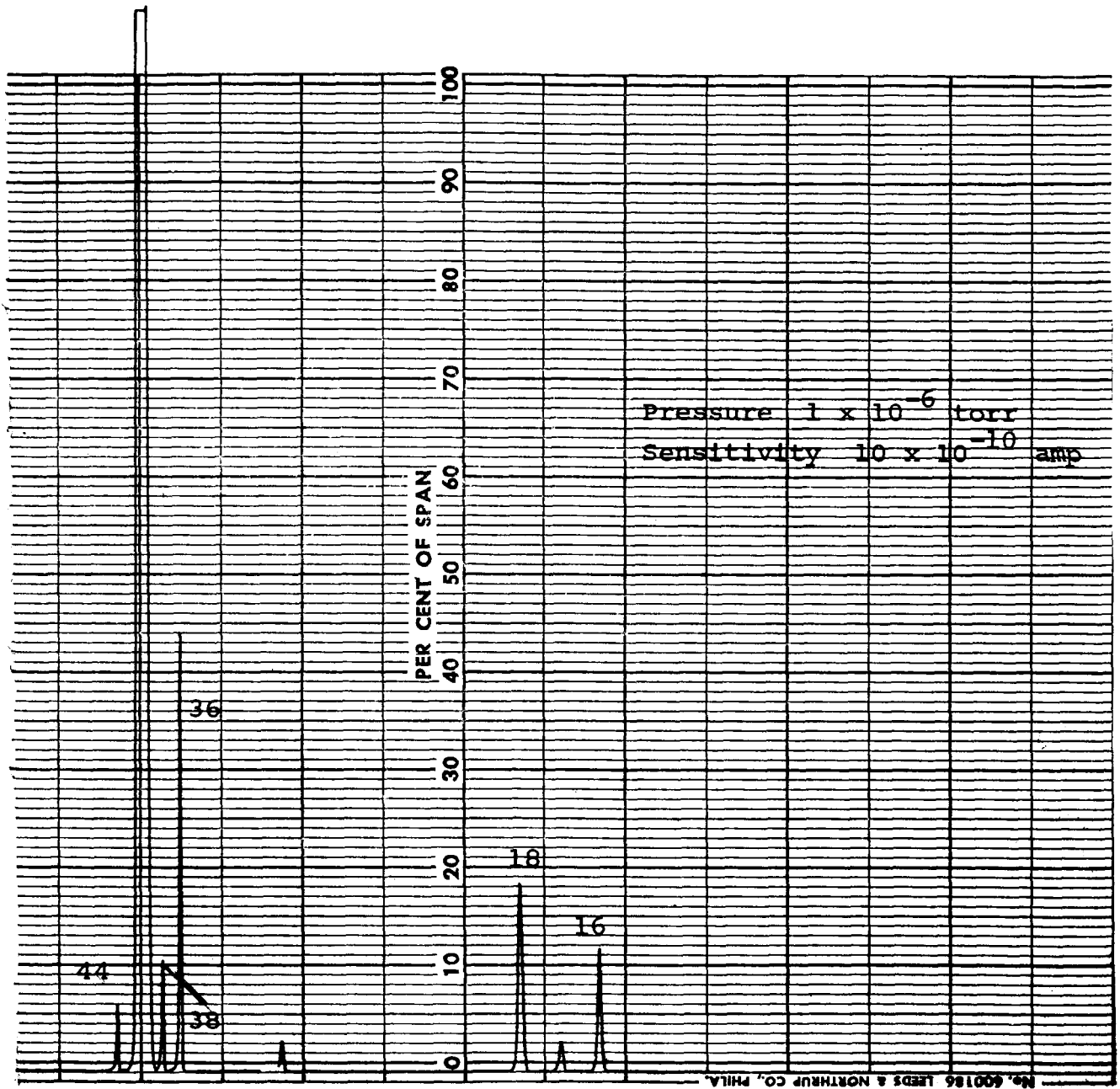


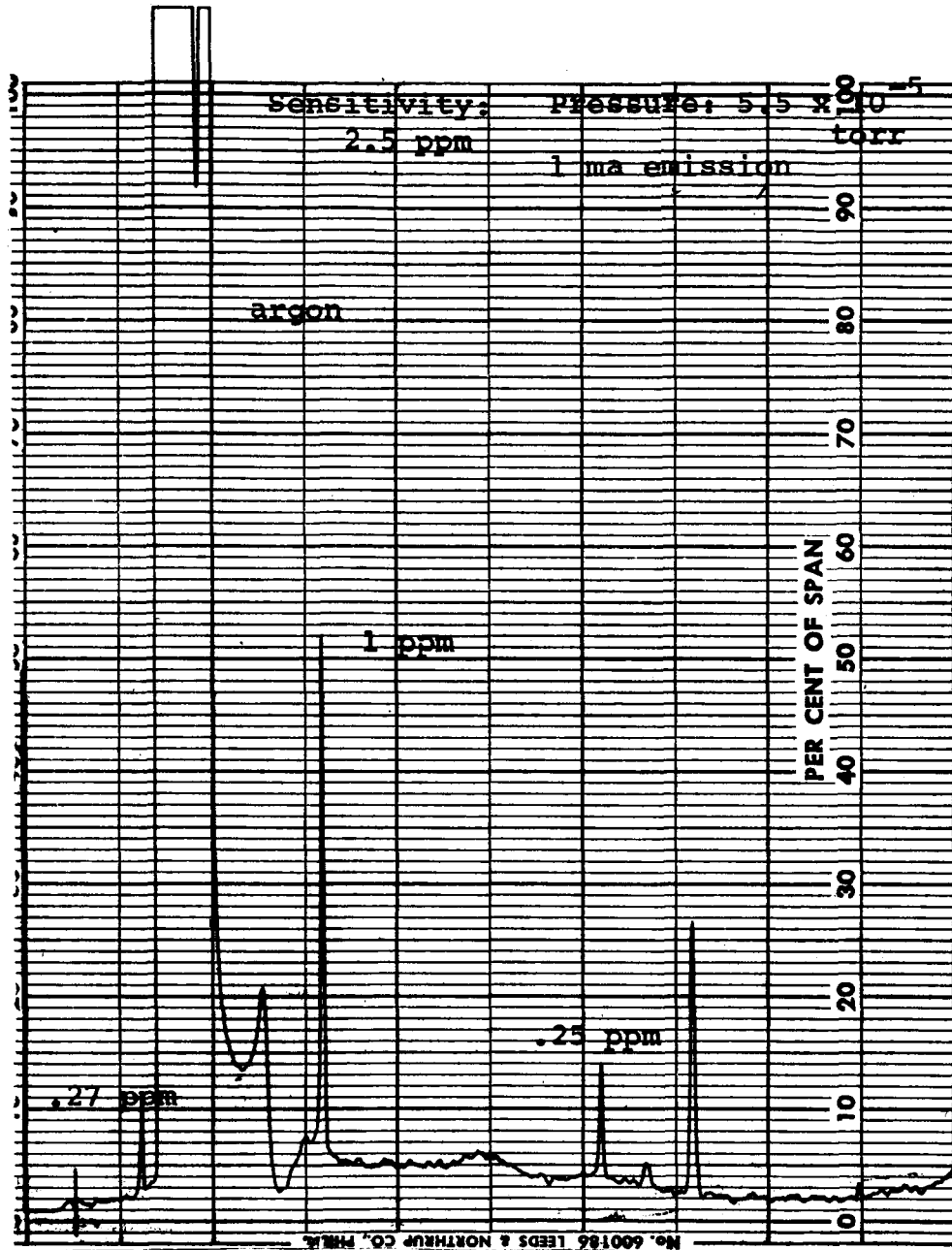
Fig. 7a

Spectra Showing Low Impurity Concentrations



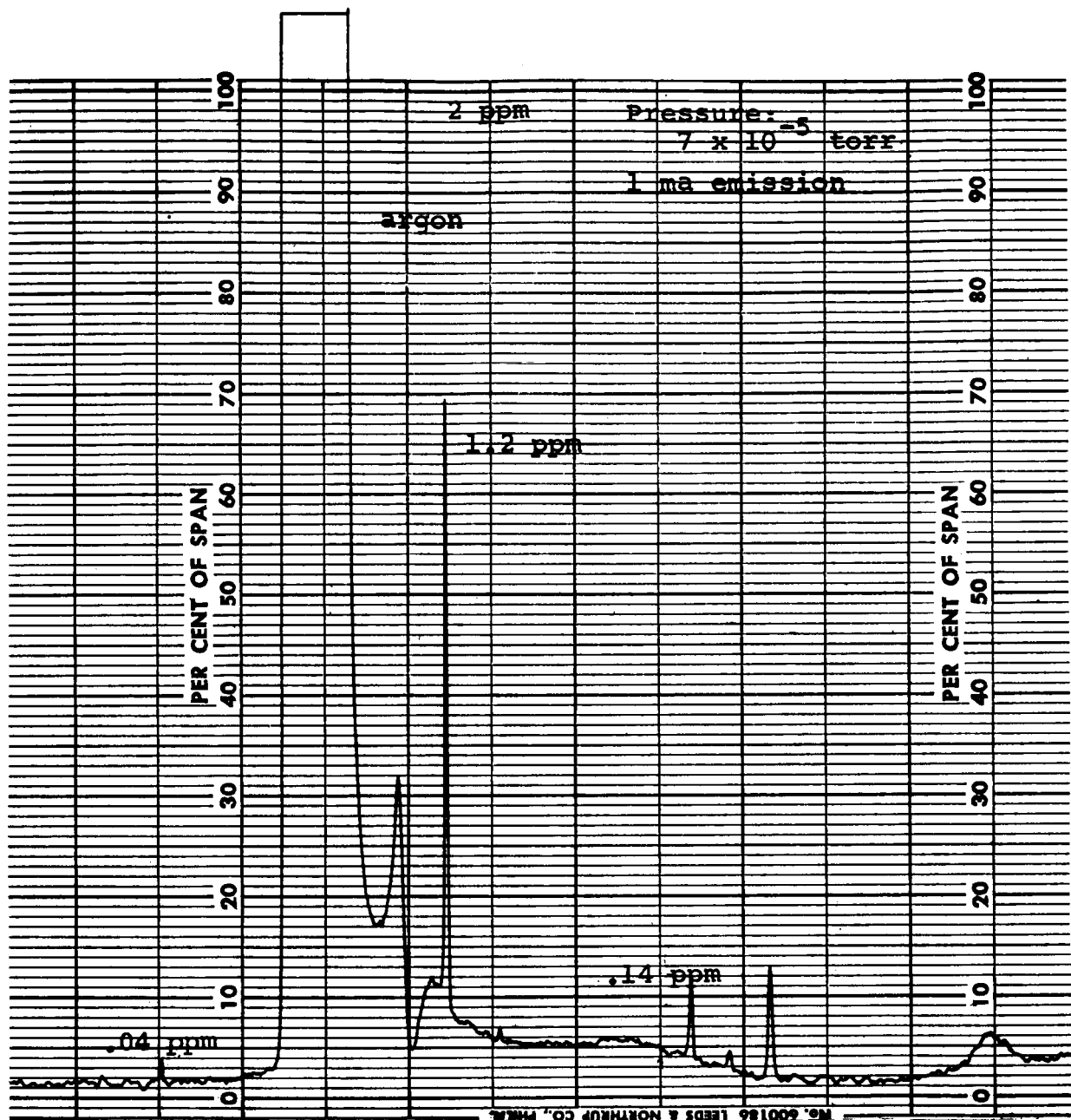
Normal Argon-Water Spectrum

Fig. 8



Spectrum of Argon with Impurities

Fig. 9



Spectrum of Argon with Impurities

Fig. 10